Experimental Determination of Concentration Dependence of Nitrogen Diffusivity in Polypropylene

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ABSTRACT: This study determines the diffusivity of nitrogen as a function of its concentration in polypropylene at 170, 180, and 190°C in the range, 0.99–6.75 MPa. Isothermal pressure decay experiments are utilized to obtain the uptake of nitrogen by polypropylene with time. These data when used with a detailed mass transfer model, and the principles of variational calculus allow the determination of the nitrogen diffusivity. It is found to be a peak function with values in the range of 3.88×10^{-9} to 12.94×10^{-9} m^2 s^{-1}. Suitable correlations are found to represent the diffusivity in terms of pressure and nitrogen concentration at the three temperatures. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2828–2834, 2011

Key words: polypropylene; nitrogen; concentration-dependent diffusivity; solubility

INTRODUCTION

Diffusion is a complex transport phenomenon, which takes place not only in polymer production during polymerization, residual monomer stripping, bulk phase separation, devolatilization[1] but also in further processing of polymers in processes such as plasticization and foaming, which result in finished and commercially useful articles. Nitrogen is an environmentally benign and inert blowing agent, the diffusivity data of which will help in a better understanding of the involved transport phenomenon.

Diffusivity is a coefficient in Fick's first law stemming from the statistical modeling of a large non-equilibrium system.[2] It is a product of the true transport property called Maxwell–Stefan diffusivity[3] and a thermodynamic nonideality factor related to the concentration of a chemical species in the medium. Hence, it is logical to expect the dependence of diffusivity of a species on its concentration. This dependence is typically strong as reported in a recent experimental study for the carbon dioxide–polyethylene system.[4] The authors used a pressure decay experiments in conjunction with a detailed mass transfer model for the natural determination of the concentration dependence. Similar experimental studies need to be carried out for other systems given the fact that only a few related experimental studies have been carried out;[5–10] all using simplified mass transfer models, and (or) ignoring the concentration effects.

The objective of this work is to experimentally determine the concentration-dependent diffusivity of nitrogen in polypropylene at elevated temperatures and pressures. For this purpose, we follow our earlier approach based on pressure decay experiments.[4] In addition to the diffusivity determination, the experimental data enable the calculation of gas solubility, which is a boundary condition of the mass transfer model. The concentration-dependent diffusivity and solubility are determined for nitrogen in polypropylene at 170, 180, and 190°C at different pressures varying from 0.99 to 6.75 MPa.

EXPERIMENTATION

The pressure decay experimentation provides a non-intrusive way to determine gas diffusivity. Following this approach, pressure versus time data were generated during isothermal diffusion of nitrogen in the underlying layer of polypropylene in a closed vessel as shown in Figure 1. The pressure cell had a concentric 4.0 cm diameter cylindrical slot at the bottom to hold a polypropylene sample. The lid of the pressure cell had a specially designed glass window allowing a complete view of the polymer surface to an external online Keyence® LKG displacement laser sensor. The sensor monitored the movement of the gas–polymer interface with the accuracy of 10 micron. A Teflon core composite Viton® O-ring was used as a sealant between the lid and the pressure cell. As shown in the figure, the cell was connected to a gas cylinder through a preheating coil. The gas cylinder was used for storing and preconditioning gas obtained from an external tank.

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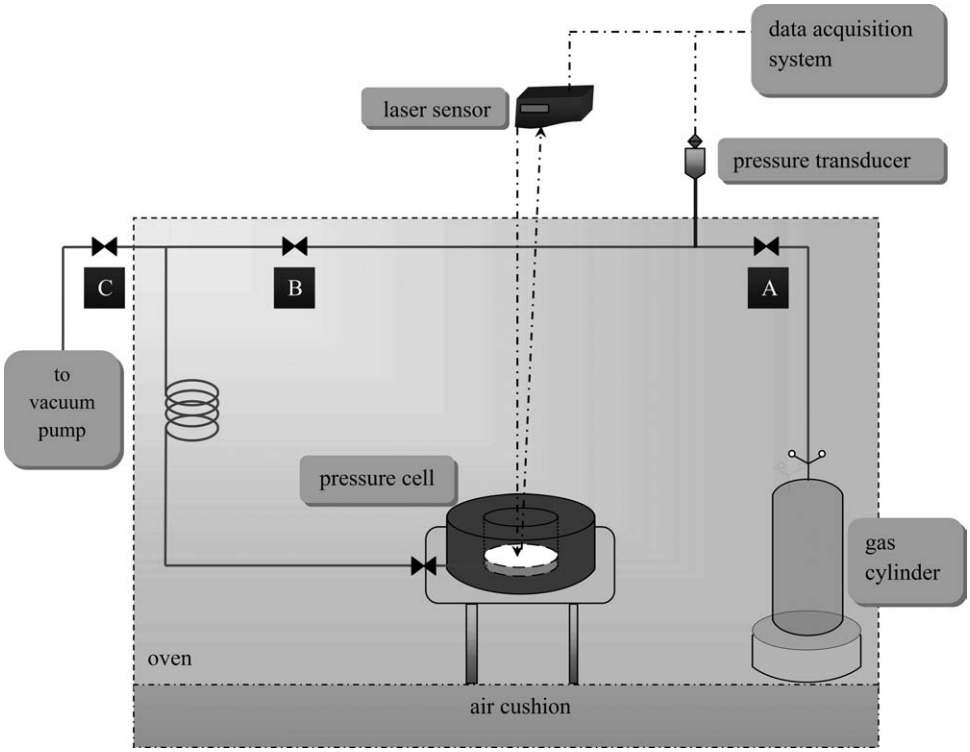

Figure 1 Schematic diagram of experimental setup.

A sensitive Paroscientific Digiquartz® pressure transmitter of ±6 Pa resolution, was connected to the tube valves A and B to measure the system pressure with time. The entire experimental apparatus setup was placed inside a large forced-air convective oven with the temperature control of ±0.5°C. The oven in turn was placed on a air table in order to keep out external vibrations from the surroundings.

Before conducting an experiment, the experimental apparatus was leak tested for 12 h. At the given operating temperature, the vessel was pressurized to one and a quarter times the given initial experimental pressure. Subsequently, valves A and C were closed, whereas valve B was opened. After successful completion of the test (i.e., if no pressure loss was discerned from the pressure sensor data for 12 h), valve C was opened to depressurize the system, and polypropylene pellets were placed in the sample slot. The whole system repressurized to detect for any pressure loss. Polypropylene pellets were melted under vacuum at the experimental temperature to form a cylindrical layer of uniform thickness. Valve C was then closed, and the laser sensor was positioned and calibrated to monitor the movement of the top surface of the polymer. The entire system was then conditioned by maintaining the temperature for 4–6 h.

The experiment was started by simultaneously opening valve B and closing valve A to introduce nitrogen into the cell as well as isolate it from the gas holder. As nitrogen diffused into the polypropylene layer, the pressure in the cell reduced with time. The pressure was recorded every 1.2 s until it became almost constant [Fig. 2(a)].[11] At that time, the mass fraction of nitrogen in the polypropylene tended to yield a uniform equilibrium value. The experiment was then terminated. The system was slowly depressurized by gradually opening valve C.

We used (i) polypropylene (melting point 160–165°C, weight average molecular weight 190,000 kg $kmol^{-1}$, and number average molecular weight 50,000 kg $kmol^{-1}$) from Sigma-Aldrich and (ii) nitrogen (more than 99.5% pure) from British Oxygen Company, Canada.

THEORY

Because polypropylene is not volatile, we can use the recorded pressure versus time, the pressure-volume-temperature data of nitrogen, and any volume change of mixing to calculate the experimental mass of nitrogen absorbed in the polypropylene layer. The experimental mass should agree with the calculated mass predicted by the mass transfer model using the diffusivity (D) of nitrogen as a function of its mass concentration (ω) in polypropylene.[12] Therefore, the criterion for the diffusivity determination is the match of the experimental and calculated masses of nitrogen in the polypropylene layer.

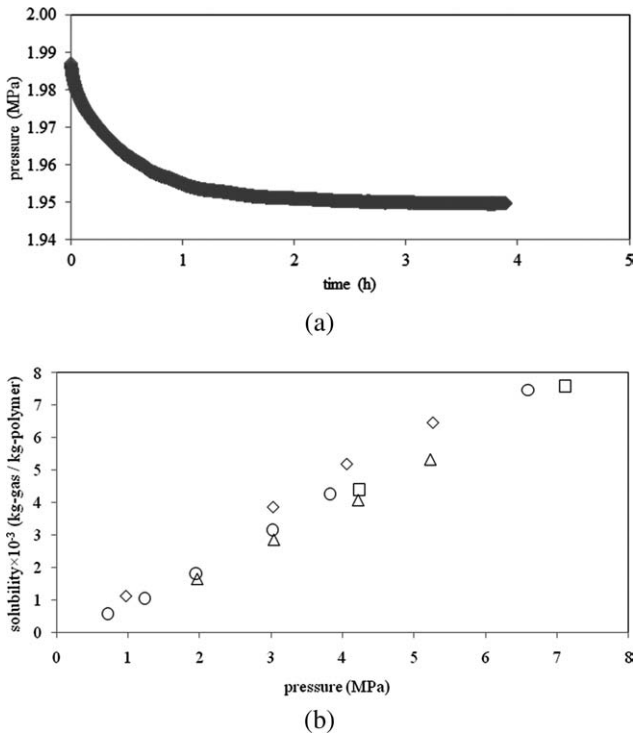

Figure 2 (a) Pressure versus time data at 180°C starting at 1.987 MPa and (b) Solubility of nitrogen in polypropylene versus pressure (◇: at 170°C, ○: at 180°C, and ◇: at 190°C in this work; □: at 180°C from Ref. [11]).

Mathematical model of mass transfer

The laser sensor did not detect any movements of the nitrogen–polypropylene interface during the experiments. This fact indicates the insignificant volume change of the polymer layer due to which the amount of the nitrogen in the polymer layer [of the order of 10^{-6} kg [Fig. (3)] has virtually no effect on its density (ρ). Hence, under the isothermal and vibration-free conditions, the convection currents in the polymer phase are obviated. Changes in volume, or displacement would be recorded only if the density of the polypropylene layer increases with the gas concentration, which being maximum at the interface decreases with depth. Thus, the transfer of nitrogen to the polypropylene layer is solely due to molecular diffusion along the vertical z-direction. Moreover, the transfer is a pure physical phenomenon as nitrogen is nonreactive with polypropylene under the experimental temperature and pressure conditions. Under these considerations, the mass balance of gas in the polymer layer is given by[4]

$$\frac{\partial \omega}{\partial t} = -\left[\frac{\partial N}{\partial z}\right] \tag{1}$$

where N is the mass flux of nitrogen. It is related to its diffusive flux,

$$j = -D\frac{\partial \omega}{\partial z} \tag{2}$$

and the bulk flux ($N_b = N$) as follows:

$$N = wN_b + j = wN + j \tag{3}$$

In eq. (3), w is the mass fraction of nitrogen in the polypropylene layer, and is given by

$$w = \frac{\omega}{\omega + \rho} \tag{4}$$

From eqs. (2)–(4)

$$N = \frac{D}{1-w}\frac{\partial \omega}{\partial z} \tag{5}$$

Substituting the above result in eq. (1) yields the mass transfer model,

$$\frac{\partial \omega}{\partial t} = D\left[1+\frac{\omega}{\rho}\right]\frac{\partial^2 \omega}{\partial z^2} + \left[\left(1+\frac{\omega}{\rho}\right)\frac{\partial D}{\partial \omega} + \frac{D}{\rho}\right]\left(\frac{\partial \omega}{\partial z}\right)^2 \equiv f \tag{6}$$

In the above model, $\omega = \omega(z, t)$ is the mass concentration of the gas in the polymer at a depth z, and a time t. The diffusivity D is a function of ω, i.e. $D = D[\omega(z, t)]$. Because there is no nitrogen in the polypropylene layer at $t = 0$,

$$\omega(z, 0) = 0; \quad 0 < z \le L \tag{7}$$

The concentration of nitrogen at the interface is known at all times, i.e.,

$$\omega(0, t) = \omega_{sat}(t); \quad 0 \le t \le T \tag{8}$$

where T is the final time. Because there is no mass transfer at the bottom of the cell,

$$\left.\frac{\partial \omega}{\partial z}\right|_{z=L} = 0; \quad 0 \le t \le L \tag{9}$$

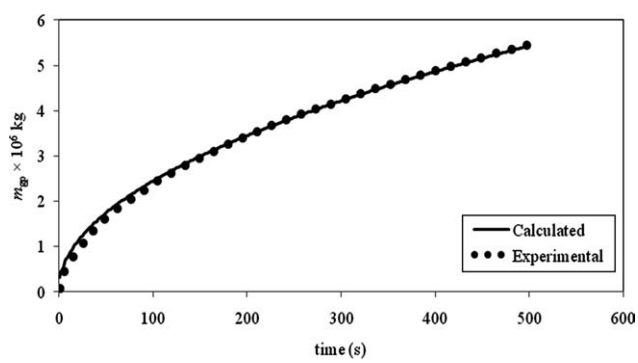

Figure 3 Experimental versus calculated value of gas mass absorbed of nitrogen in polypropylene.

Equations (7)–(9) are the initial and boundary conditions for eq. (6). The above mass transfer model forms the basis of diffusivity determination as described next.

The objective

The diffusivity of nitrogen in polypropylene should be such that the following objective functional

$$I = \int_0^T \left[m_{\mathrm{gp,m}}(t) - m_{\mathrm{gp,e}}(t)\right]^2 \mathrm{d}t \tag{10}$$

is minimum. Here $m_{\mathrm{gp,e}}(t)$ is the experimental mass of gas absorbed in the polymer, whereas $m_{\mathrm{gp,m}}(t)$ is the mass of nitrogen absorbed in the polymer layer as predicted in the mass transfer model given by eqs. (6)–(9). The model-predicted mass is

$$m_{\mathrm{gp,m}}(t) = \int_0^L \omega(z,t) A \mathrm{d}z \tag{11}$$

where L is the depth of the polypropylene layer of cross-sectional area A. Note that $\omega(z,t)$ is given by highly nonlinear partial differential equation, eq. (6), which carries $D(\omega)$ as the optimization or control function. The necessary condition for the constrained minimum of I is

$$\lambda \frac{\partial f}{\partial D} = 0; \quad 0 \le z \le L, \quad 0 \le t \le T \tag{12}$$

subject to the satisfaction of eq. (6) as well as the equation for the adjoint variable, $\lambda(z,t)$, given by [4]

$$\begin{aligned} \frac{\partial \lambda}{\partial t} &= 2A(m_{\mathrm{gp,mod}} - m_{\mathrm{gp,e}}) \\ &+ \frac{\lambda}{\rho}\frac{\partial D}{\partial \omega}\left(\frac{\partial \omega}{\partial z}\right)^2 + \left(1 + \frac{\omega}{\rho}\right) \\ &\times \left[\lambda \frac{\partial D}{\partial \omega}\frac{\partial^2 \omega}{\partial z^2} + \lambda \frac{\partial^2 D}{\partial \omega^2}\left(\frac{\partial \omega}{\partial z}\right)^2 - D\frac{\partial^2 \lambda}{\partial z^2}\right] \end{aligned} \tag{13}$$

Equation (13) has the initial condition,

$$\lambda(z,T) = 0 \quad \forall z: \quad 0 < z \le L \tag{14}$$

and the two boundary conditions,

$$\lambda(L,t) = 0; \quad 0 \le t \le T \tag{15}$$

Along with the mass transfer model of the experimental diffusion process, eqs. (12)–(16) constitute the necessary conditions for the minimum of the augmented objective functional formed by incorporating the model to I given by eq. (10). The minimum corresponds to the desired diffusivity versus concentration function. Further details may be found in Tendulkar et al.[4] The left-hand side of eq. (12) is the variational derivative of the augmented objective functional with respect to diffusivity. At each value of gas concentration, this derivative provides the improvement in diffusivity required to minimize the objective functional. Hence, the diffusivity versus concentration function evolves with iterative calculations to the final desired value.

Iterative algorithm for diffusivity calculation

The diffusivity of nitrogen in polypropylene was calculated by integrating eq. (6) with an initially guessed diffusivity. The results were used during the backward integration of eq. (13) to obtain J from eq. (12), and apply it for gradient corrections to the diffusivity. These corrective steps were iterated until the cessation of any reduction in I. The calculation of I requires $m_{\mathrm{gp,e}}$ (t), which was obtained from the experimental pressure versus time data for about 2% pressure decay in conjunction with the PVT relationship of the gas.[13]

The value of $m_{\mathrm{gp,e}}$ (t) at the final pressure corresponding to a relatively infinite time yields the saturation mass concentration of nitrogen, $\omega_{\mathrm{sat}}[P(t)]$. It provides the boundary condition, i.e. eq. (8). $\omega_{\mathrm{sat}}(P)$ was determined at the three experimental temperatures by performing 14 experiments for extended time durations. The obtained values are provided in Figure 2(b).

Eqs. (6) and (13) were numerically integrated after applying second-order finite difference approximations along the z direction. The time period for the integrations was carefully selected to limit pressure decay to less than 2% of the initial pressure. The fifth-order adaptive step Runge-Kutta-Fehlberg method was utilized with Cash-Karp parameters.[14] The diffusivity was considered to be discrete function, $D(\omega)$, at specified nitrogen concentrations between zero and the maximum, at time $t = 0$, for an experiment. For the initial guess, $D(\omega)$ was taken to be a uniform step function as large as possible without causing $m_{\mathrm{gp,m}}(t)$ to intersect $m_{\mathrm{gp,e}}(t)$. The values of the variational derivative, $J(\omega)$, were time-averaged before their usage for the gradient correction in $D(\omega)$ by Broyden-Fletcher-Goldfarb-Shanno algorithm. Further details are provided elsewhere.[4]

Table I provides the parameters used in the calculations. The density of the polypropylene sample is based on its mass, diameter, and thickness. The thickness was measured by the laser sensor during the experiments at the elevated temperatures. The number of grid points and diffusivity values and the

TABLE I
Parameters Used in the Diffusivity Calculations

Parameter	Value
Mass of polymer	5×10^{-3} kg
Density of polymer	763.417 kg m^{-3}
Diameter of polymer sample	4×10^{-2} m
Thickness of polymer sample	5.2119×10^{-3} m
Initial guess for D	6×10^{-10} m^2/s
No. of D vs. ω points	75
No. of grid points along the sample depth	60

accuracy of integrations were determined after varying those parameters to the point when the changes in the solution became insignificant. The experimental and the optimally calculated values of gas mass absorbed in polymer agreed well as shown in Figure 3.

RESULTS AND DISCUSSION

Using the aforementioned experiments and calculations, we determined the concentration-dependent diffusivity and solubility of nitrogen in polypropylene at 170, 180, and 190°C in the pressure range, 0.99–6.75 MPa. Changes in diffusivity values were found be insignificant for ±2% variation in the gas phase volume, or measured pressure.

Figures 4–7 present the diffusivity versus concentration functions of nitrogen thus obtained. The concentration-averaged diffusivity values are provided in Table II. Because the equilibrium concentration of nitrogen in polypropylene increases with pressure but decreases with temperature, the concentration range increases with pressure (Figs. 4–6) but decreases with temperature (Fig. 7).

Effect of pressure on diffusivity

The diffusivity versus concentration for different pressures is plotted in Figures 4–6 at 170, 180, and 190°C, respectively. The diffusivity is generally of the order of 10^{-9} m^2 s^{-1}. It is observed that the maximal concentration (at the peak diffusivity) increases with pressure at all the three temperatures. Hence, as pressure increases at a fixed temperature, the diffusivity (i.e. the maximum mass flux per unit concentration gradient) peaks at a higher nitrogen concentration. Therefore, higher concentration is required at higher pressure to attain the maximum possible mass transfer at the given temperature.

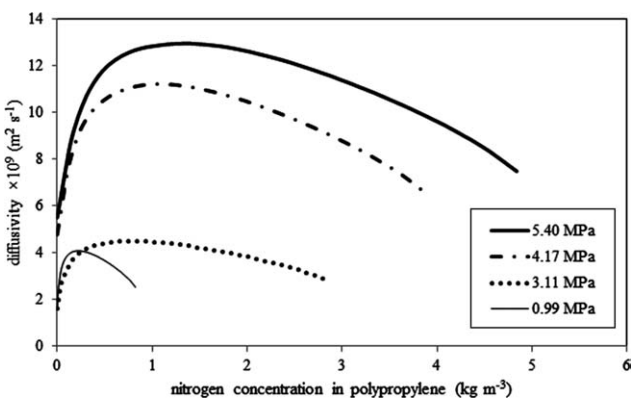

Figure 4 Diffusivity of nitrogen as a function of concentration at 170°C and different pressures.

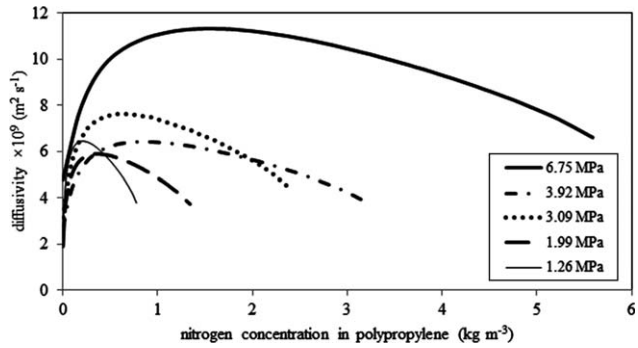

Figure 5 Diffusivity of nitrogen as a function of concentration at 180°C and different pressures.

Besides the above behavior, the effect of pressure on diffusivity (including the peak diffusivity) is found to be nonlinear with the following two exceptions:

1. At 170°C, the diffusivity of nitrogen (Fig. 4) increases with pressure for nitrogen concentration greater than 0.3 kg m^{-3}.
2. At 180°C, the diffusivity nitrogen (Fig. 5) increases with pressure for the concentration in the range 0.4–1.9 kg m^{-3}.

In one case at 170°C, the relative change in diffusivity is observed to be considerably larger than the relative change in pressure. As seen in Figure 4, the average diffusivity at 4.17 MPa is more than twice its value than that at 3.11 MPa. A similar but reverse trend is observed at 190°C (Fig. 6). The average diffusivity at 4.31 MPa is in fact about half of the average diffusivity at 3.11 MPa.

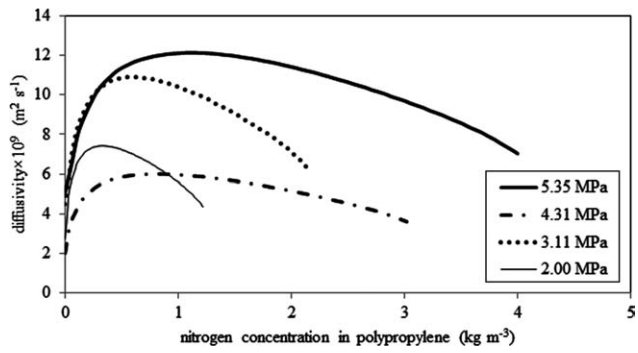

Figure 6 Diffusivity of nitrogen as a function of concentration at 190°C and different pressures.

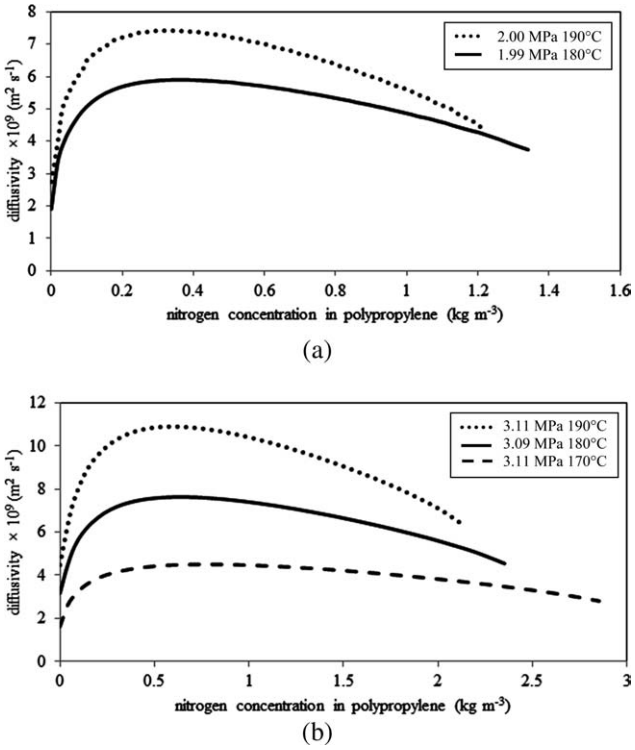

Figure 7 **(a)** Effect of temperature on nitrogen diffusivity near 2 MPa and **(b)** Effect of temperature on nitrogen diffusivity near 3 MPa.

At all the temperatures, two or more diffusivity versus concentration graphs cross each other, thereby implying same diffusivity at a given concentration at different pressures. The crossing points are the transitions between two opposites diffusivity versus pressure trends. For example, at 170°C, the diffusivity at 3.11 MPa is higher than that at 0.99 MPa for concentration less than 0.3 kg·m^{-3}. Beyond this concentration, the diffusivity trend is opposite.

The nonlinear effect of pressure on diffusivity may be imputed to the interplay of different phenomena. Increase in pressure gives rise to more frequent intermolecular collisions but at reduced intermolecular distances. Although increased molecular collisions promote gas diffusion, the shorter intermolecular distances do the opposite. Subject to the prevailing phenomenon, the diffusivity either increases or decreases with pressure at a given temperature. The high diffusivity at 4.17 MPa compared to that at 3.11 MPa at 170°C suggests that the change in the polymer matrix structure may not precluded. The possibility of this phenomenon needs to be further investigated to gain better insight of the effect of pressure on diffusivity.

TABLE II
The Concentration-Averaged Diffusivity of Nitrogen in Polypropylene at Different Temperatures and Pressures

Temp. (°C)	Pressure (MPa)	Average diffusivity × 10^9 (m^2 s^{-1})
	0.99	3.53
170	3.11	3.90
	4.17	9.55
	5.40	10.99
	1.26	5.49
180	1.99	5.09
	3.09	5.23
	3.92	5.50
	6.75	9.65
	2.00	6.32
190	3.11	9.26
	4.31	5.12
	5.35	10.32

TABLE III
Parameters for the Diffusivity Correlation, eq. (17)

Parameters	170°C	180°C	190°C
α_o	3.547	5.216	−129.486
α_1	−45.259	2.722	386.549
α_2	−0.055	1.171	2.104
α_3	61.666	−6.144	−345.414
α_4	−2.752	−6.900	−22.639
α_5	5.279	4.315	19.430
α_6	−20.044	2.592	97.386
α_7	1.917	0.819	3.127
α_8	−5.971	−0.337	4.678
α_9	3.042	0.703	−6.425
r^2-coefficient of determination	0.987	0.914	0.969
Fit standard error	0.394	0.593	0.446
F-statistic	3026	579	960

Effect of temperature on diffusivity

Unlike the pressure effect, the effect of temperature on diffusivity (Fig. 7) is observed to be straightforward in the vicinity of 2 and 3.1 MPa. This effect is same as typically observed for other polymer systems.[11,15–18] At both pressures, the diffusivity of nitrogen is higher at a higher temperature. The increase in the diffusivity with temperature may be ascribed to the reduction in polymer viscosity, lowering of the activation energy, and increase in molecular motion. These phenomena help increase the transfer of nitrogen in the polymer matrix. The increase in the diffusivity is found to gradually decrease with the nitrogen concentration. A likely reason is that the gradual crowding of nitrogen molecules in the polymer matrix begins to restrict their transfer after a certain threshold.

The solubility of nitrogen in polypropylene is plotted in Figure 2(b). The solubility increased almost linearly with increasing pressure, and decreased with temperature. This type of pressure and temperature dependence of solubility is usually observed in similar gas–polymer systems. As shown in the

figure, the solubility results of this work at 180°C compare well the data generated in a previous study.[11]

Diffusivity correlations

Finally, the diffusivity results obtained in this work were correlated. Using Table Curve 3d^{TM}, the diffusivity of nitrogen at a given temperature was fitted in terms of its concentration in polypropylene, and pressure. The best function with as few parameters as possible was found to be:

$$\lambda(0,t) = 0; \quad 0 \le t \le T \tag{16}$$

In the above equation, D is in 10^9 m^2 s^{-1}, P is in MPa, and ω is in kg m^{-3}. Table III lists the fitting parameters and details for eq. (17) at 170, 180, and 190°C.

CONCLUSIONS

This article determined the concentration-dependent diffusivity and solubility of nitrogen in polypropylene at temperatures of 170, 180, and 190°C, and pressure in the range 0.99–6.75 MPa. The pressure decay data were used in conjunction with a detailed mass transfer model to calculate the diffusivity of nitrogen as a function of its concentration in polypropylene. Nitrogen solubility was also determined from the data. The results show that nitrogen solubility increased almost linearly with pressure but decreased with temperature. The nitrogen diffusivities in polypropylene were found to be strong peak functions of nitrogen concentration, and generally of the order 10^{-9} m^2 s^{-1}. Empirical correlations were derived for the diffusivity of nitrogen as a function of its concentration and pressure at the three temperatures.

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NOMENCLATURE

a_i	Parameters of eq. (17); ($i = 0,1,\ldots,9$)
A	Cross-section area of the polymer layer, m^2
d	Internal diameter of the pressure vessel, m
D	Diffusivity of gas in polymer, m^2 s^{-1}
I	Objective functional
J	Variational derivative
K	Augmented objective functional
L	Thickness of the polypropylene layer, m
$m_{gp,m}$	Calculated mass of nitrogen absorbed in the polypropylene layer, kg
$m_{gp,e}$	Experimental mass of nitrogen absorbed in the polypropylene layer, kg
M_g	Molar mass of nitrogen, kg kmol^{-1}
P	Pressure, MPa
T	Total experimental run time, s
w	Mass fraction of gas in polymer layer
z	Depth in the polymer layer, m
ρ	Density of polymer sample, kg m^{-3}
λ	Adjoint variable
ω	Mass concentration of nitrogen in the polypropylene layer, kg·m^{-3}
ω_{sat}	Saturated ω, kg m^{-3}

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